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CROSS SECTIONS FOR THE PROI)UCTION OF ENERGETIC CATIONS BY ELECTRON IMPACT ON N_2 AND CO_2

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Abstract: Dissociative ionization cross sections for the production of singly charged energetic ions by electron impact on N_2 and CO_2 have been measured. The ions were divided into two groups: one with energies less than 1 CV and the other with energies greater than 1 eV. The ions detected were N+ from N_2 and C^+, 0', and CO^+ from CO_2. The electron impact energy ranged from 40 eV to 1000 eV for N_2 and from 30 eV to 500 eV for CO_2. Cross sections for the product ion of slow and fast fragment ions are presented for the first time.

Introduction

When an electron collides with a molecule the following two types of processes, among others, can take place:

$$e + MN \rightarrow M^{+} + N + 2e \qquad \ldots(1)$$
$$\rightarrow M^{+} + N^{+} + 3e \qquad \ldots(2)$$

where MN is a molecule with fragments M and N, + sign represents a singly ionized species. The above two processes can occur in a number of ways. Typically the molecule is excited from its ground state to a singly or doubly ionized repulsive or pre-dissociative state which subsequently dissociates to give rise to fragment ions. The ions resulting from the process of pre-dissociation carry a small amount of energy and are usually referred to as thermal, whereas those coming from direct ionization to repulsive states have much larger energy. Cross sections for the formation of energetic ions and their angular distributions have importance in radiation chemistry and dosimetry. They are also helpful in the interpretation of mass spectra of ions generated by various mass spectrometers. Furthermore, it is known that kinetic energies of fragment ions are effective in controlling the temperature of their environment. Therefore, an accurate knowledge of the kinetic energy spectra of the fragment ions, their angular distributions and their abundances is important. A close look at the previously published literature shows that except for a few selected molecules these data are not readily available. This is especially true for the cross section values of energetic ions. The only measured data available in the past have been of Rapp et al, [1].

The lack of data on the cross sections for the production of energetic ions by electron impact on molecules and their kinetic energy spectra prompted us to undertake a systematic study of this subject. We have developed instrumentation and methods to accomplish this aim. As a first step in this direction we have investigated N_2 and CO_2 molecules.

Kinetic energy spectra for N^{+} resulting from the dissociative ionization of N_2 have been measured by several workers in the past. Noteworthy among them are Kieffer and Van Brunt [2], Deleanu and Stockdale [3], Crowe and McConkey [4], Kollman [5], Locht et al. [6] and Feldmeir et al. [7]. The kinetic energy spectra and angular distributions for ionic fragments CO^{+} and O^{+} resulting from the dissociation of CO_2 by electron impact have been reported by Zhukov et al. [8] and Crowe and McConkey [9].

The mechanism for the production of low energy (below 1 eV) ions from the predissociation of N_2^{+} ($C^2\Sigma u^{+}$ state) was first proposed by Smyth et al. [10] and later on confirmed by Locht et al. [6], Wankenne et al. [11] and Kieffer and Van Brunt [2]. For CO_2 the only recent data are of Zhukov et al. [8]. They have reported the production of thermal ions of O^{+} and CO^{+} from CO_2 by electron impact and have discussed the probable mechanisms of their formation.

In the following our experimental set up, data reduction techniques and results will be presented.

Apparatus and Data Reduction

Figure 1 shows the schematic diagram of the experimental arrangement used in the present measurements. It ut ilizes a crossed electron bean-molecular beam collision geometry and consists of a time-of-flight mass spectrometer [TOFMS] [12,13], a pulsed-electron gun, a Faraday cup, a capillary array and the conventions] electronics. An energy selected electron beam collides with a beam of molecules of interest at 90”. The molecular beam is formed by flowing the gas through a capillary array. Ions produced in the interaction region arc extracted into the TOFMS. The production and extraction of ions are done by a synchronized pulse technique [12,13]. The ext ratted ions are then focussed and transported by the TOFMS, which consists of five equi - spaced cylindrical lenses of same diameter but of different lengths, onto a charged particle detector. During the production of ions, the extraction voltage (- 50 V) on the first lens of the TOFMS is brought down to the ground potential by a fast positive pulse of the same magnitude while the rest of the lenses are kept at suitable voltages. Each detected ion gives rise to an electrical pulse of about 20 mV amplitude which is inci eased by a fast amplifier to about 2V. This pulse is then fed to a time delay unit which can delay it from 1 nsec. to 1 msec. The delayed pulse passes through a constant fraction discriminator (CFC) whose output is then fed to the stop terminal of a time to amplitude converter/single channel anal yzer (TAC/SCA). A start pulse to the TAC/SCA is provided by a pulse generator employed for pulsing the electron beam. The time difference (AT) between the start and stop pulses is equal to the t ime of flight of the ion from the coll ision region to the detector. For a particular ion, this time of flight depends on its kinetic energy. The AT is converted by the TAC into an electrical pulse whose amplitude is proportional to the AT. These pulses of varying amplitudes are then stored in a pulse height analyzer (PHA) which displays thcm as a function of the AT. A typical record of pulses is shown in figures 2a and 2b for N^+ ions for an electron impact energy of 70 eV. in these TOF spectra, two groups of N‘ ions are clearly separated. The sharp peak corresponds to the slow ions where as the broad peak represents the distribution of energetic ions which arrive at the detector early,

The main aim of this work is to derive values of cross sections for the energetic ions. The TOF provides us the kinet ic energy spectra of fragment ions. The relative intensities of ions are convoluted with the transmission efficiency function of the TOFMS. This transmission efficiency function strongly depends on the kinetic energy of the ions and its determination is not an easy task. However, the fragment ions that are born with energies close to thermal should have the same transmission as the parent ion. In fact, this has been verified experimentally in the following way. Spectra in figures 2a and 3a are recorded with crossed-beam geometry whereas the spectra shown in figures 2b and 3b are recorded under the same experimental conditions but in the static gas geometry in which case the whole chamber is filled with the gas of interest. The count rate in the crossed-beams mode is about 20 times higher than the count rate in the static gas mode. However, when the intensity of the TOF spectrum of static gas mode is normalized to that of crossed-beams mode with respect to the parent ions, the peak values of all slow fragments also match with each other but not the fast ones. This is due to the fact that all slow ions are collected, irrespective of the co] 1 is ion geometry. However, some of the fast ones escape the complete collection in the static gas geometry in spite of a large ext action field. in addition to the kinetic energy dependence, there is also a mass dependent Transmission factor for various ions. This factor was obtained by a procedure described by Krishnakumar and Srivastava [14] where the relative flow technique and the well known cross sections of rare gas atoms were used for the determination of the mass transmission efficiency of the system.

From the cross beams TOF spectra, one can obtain the ratios of the intensities of thermal fragments to the parent ions. From the knowledge of the ionization cross section values of the parent ion available in the literature, values of cross sections, σ_d^{slow}, of the slow fragments can be obtained. in the case of N_2, the ratio of $\sigma_d^{slow}/\sigma(N_2)$ is multiplied by the previously measured [15] value of cross section for the production of N_2^+ . Similarly, the ionization cross section values of Orient and Srivastava [16] for the production of CO_2^+ by electron impact were used for multiplying the ratio σ_d "("v $(CO^+)/\sigma(CO_2)$ and $\sigma_d^{slow}(O^+)/\sigma(CO_2)$. These cross sections are, in turn, used to obtain the cross sections, σ_d^{fast}, of energetic fragment ions by using the following equation:

$$\sigma_d^{fast} = \sigma_d - \sigma_d^{slow}$$

where σ_d are dissociative ionization cross sections (a sum of fast and slow ionization cross sections) measured previously [15, 16],

Results and Discussion:

Figures 2 and 3 show the time of flight spectra of N_2 at an electron impact energy of E_o = 70 eV and of CO_2 at E_o = 300 eV, respectively. Figures 2(a) and 3(a) represent the crossed beam results and figures Z(b) and 3(b) provide data for static collision geometry.

In the N+ TOF spectrum there are two features: a and b. The feature b represents the intensity of slow (<1 eV) N+ ions which result from the pre-dissociative state of $N_2\,(C^2\Sigma_u^+)$ and the feature a consists of energet ic N" ions which have been found to possess maximum kinetic energy at 3 and 7 CV by several authors in the past [2,7].

The above measurements were also made at electron impact energies (E_o) of 50, 75, 100, 150, 200, 300, 400, 500, 600, 700, 800, 900 and 1000 eV.

In the CO_2 TOF spectrum (fig. 3) the fragment ions arc designated as (a) C^+, (b)fast O', (c)slow 0^+, (d) $C0^{2i}$, (c) fast CO^+, (f) slow CO^+ and (g) CO,'. The m/e values of these peaks were obtained by calibrating the TOF spectrum with the masses of rare gases as described in ref. [14].

Recentl y Zhukov et al. [8] have measured kinetic energies of O^+ and CO^+ fragment ions result ing from the dissociation of CO_2 by electron impact. They have reported that the energy dist ribut ion of O" shows slow ions with maximum intensity around O eV and energetic 0^+ ions with maximum at approximately 1.3 eV. Similarly CO^+ ions were found to have maximum kinetic energy around 1.8 eV. Therefore, in our TOF spectrum of $C0_2$ in figure 3, the peaks b and c are assigned to O^{+} ions of 1.3 eV and O eV, respectively, and c and f are of CO^{+} ions at 1.8 eV and OeV, respectively. The TOF spectra for CO_2 dissociative ionization were recorded at various electron impact energies from 40 to 500 eV.

As explained in the previous section, from the intensit y ratios of fragment ions to the molecular ions the cross sections were derived for the production of all fragment ions. They were then added together to obtain total ionization cross sections for the generation of all ions from N_2 and CO_2, respectively. These cross sections are compared with the total ionization cross sections published by Rapp et al. [17] and are shown in fig. 4. As can be seen in this figure, the agreement between the two results is good. This fact indicates that with the present ion extraction fields we can collect all energetic ions (at least up to 10 eV energies) with almost unit efficiency.

In fig. 5 filled circles show the percentage of N^{+} ions which are born with K .E. less than 1 CV with respect to the total ionization cross section of N_2. As was explained in the previous section, cross sections for energetic ions were derived by two different methods: one by obtaining the intensity ratios of fast N" ions with respect to the N_2^{+} ions and the other by subtracting the cross sections for the production of slow N' ions from the total dissociative ionization cross sections published by Krishnakumar and Srivastava [15]. The results, in principle, should agree with each other. This is indeed the case. They are shown in fig. 5 by open triangles and open squares, respective] y. It can be seen that the percentage of the slow ions is approximately 5 % of the total ionization in the high impact energy region whereas the percentage of fast ions is about 19%. It implies that the total dissociation for N' production is about 25% of the total ionization (sum of cross sections for the production of all ionic species). The data of Rapp et al. [1] for ions with energies 0.25 eV (open diamonds) arc also shown in fig. 5. l'heir results agree well, within the error limits of each experiment, with the present measurements when the cross sections of both fast (open triangles) and slow (filled circles) ions arc added together.

In fig. 6 the percentage of all fragment ions with respect to the total ionization is shown for CO_2. Open circles represent the percentage of ions with energies estimated to be less than 1 cV, filled circles represent the ions with energies greater than 1 eV and filled triangles are the data of Rapp et al. [1] for the ions with energies >0.25 eV. The percentage of the slow ions (C-' + O^{+} + CO-') is about 15% of the total ionization in the high impact energy (larger than about 100 eV) range. The intensity of fast ions is about the same as the intensity of the slow ions. The percentage of fast ions having energies >0.25 eV, reported by Rapp et al. [1], is about 25% to the total ionization. However, as in the case of N_2, if the values for slow and fast ions are added together then the agreement between the two measurements is satisfactory. At energies less than 100 CV our data for slow ions do not vary with electron impact energy as smoothly as the data of Rapp et al.

Conclusions

Time of flight spectra for fragment ions produced by electron impact on N_2 and CO_2 were obtained at various electron impact energies. The features for high and low energy fragments are identified with the kinetic energy distributions reported in the literature. From the TOF spectra we provide cross sections for slow as well as for the fast fragment ions. Total ionization cross sections are also obtained for N_2 and CO_2. The present values of total ionization cross sections are in good agreement with the values reported by Rapp et al. [17]. The cross sect ions for slow and fast fragment ions, separately, are reported for the first time.

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Figure Captions

Figure 1. Schematic diagram of the experimental arrangement.

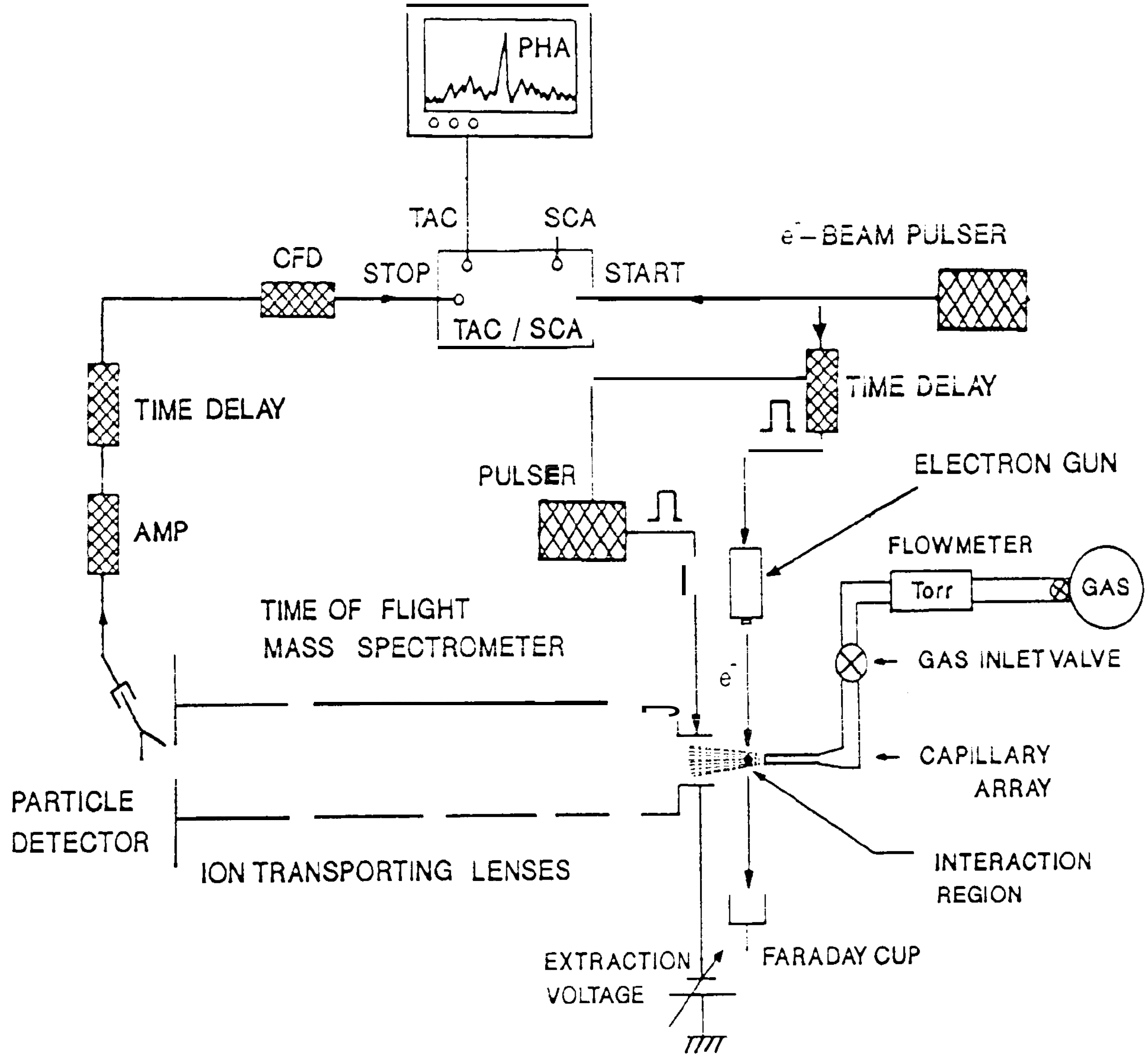
Figure 2a and 2b. TOF spectra, showing N_2 fragmentation at 70 eV impact energy for the crossed-beam and static beam geometries, respectively.

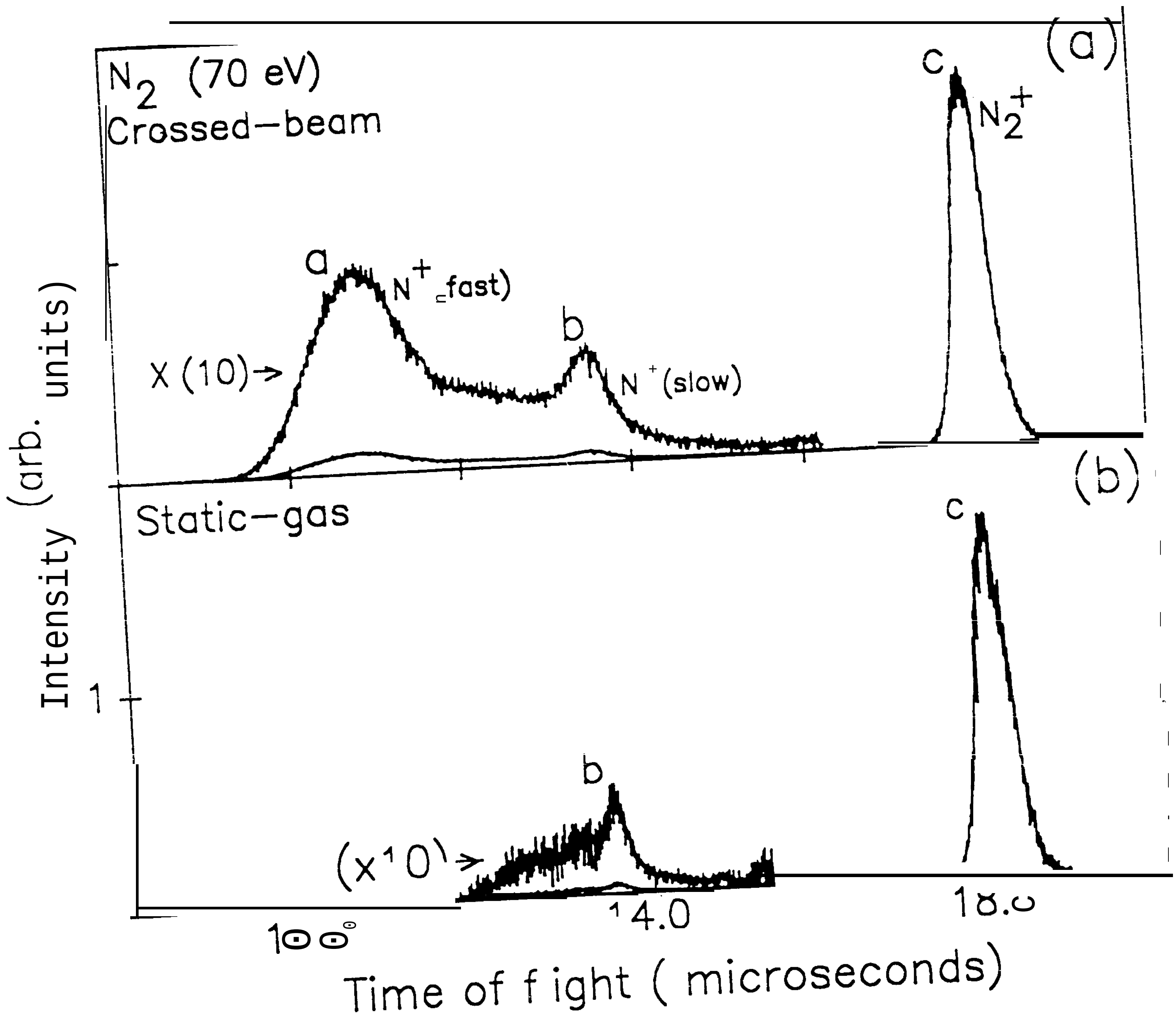
Figure 3a and 3b. Same as figure 2 for CO_2 at 300 eV electron impact energy

Figure 4. Total ionization cross section as a function of electron impact energy for N_2: o, present; ● , values of ref. 16 and for CO_2: A, present; A values of ref.1 7,

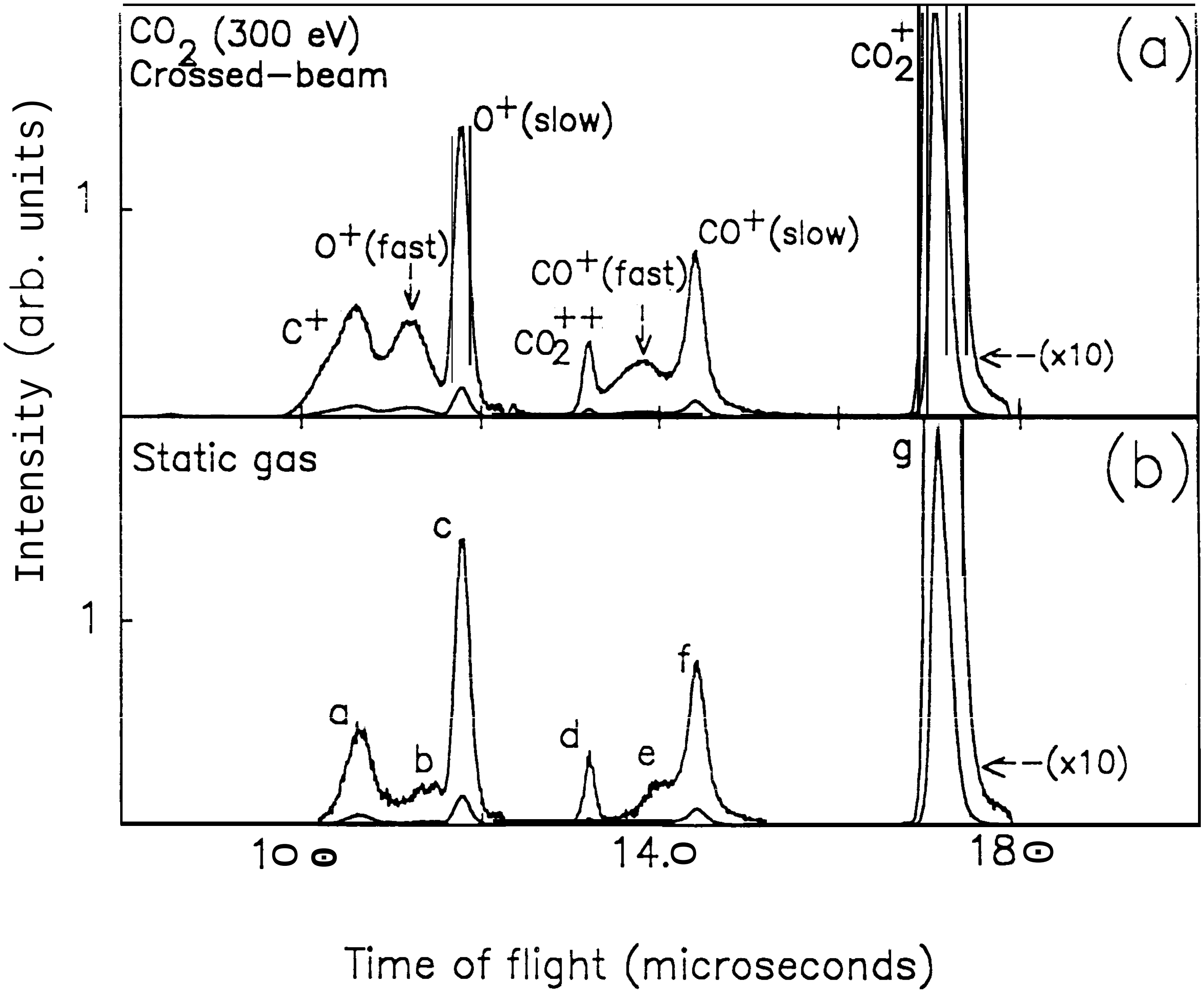
Figure 5. % of total ionization as a function of electron impact energy: O for N” ions which are born with energies E< leV; □ and A, N’ ions which are born with energies E> leV; o, N^+ ions which arc born with energies E > 025eV (ref. 1).

Figure 6. % of total ionization as a function of electron impact energy: O for (C-’ + O’ + CO^+) ions which arc born with energies E < leV; ● , for (C^+ + 0^+-1- CO-’) ions which are born with energies E > leV; A, for (C^+ + 0^+ + CO’) ions which are born with energies E < 0.25eV (ref. 1).

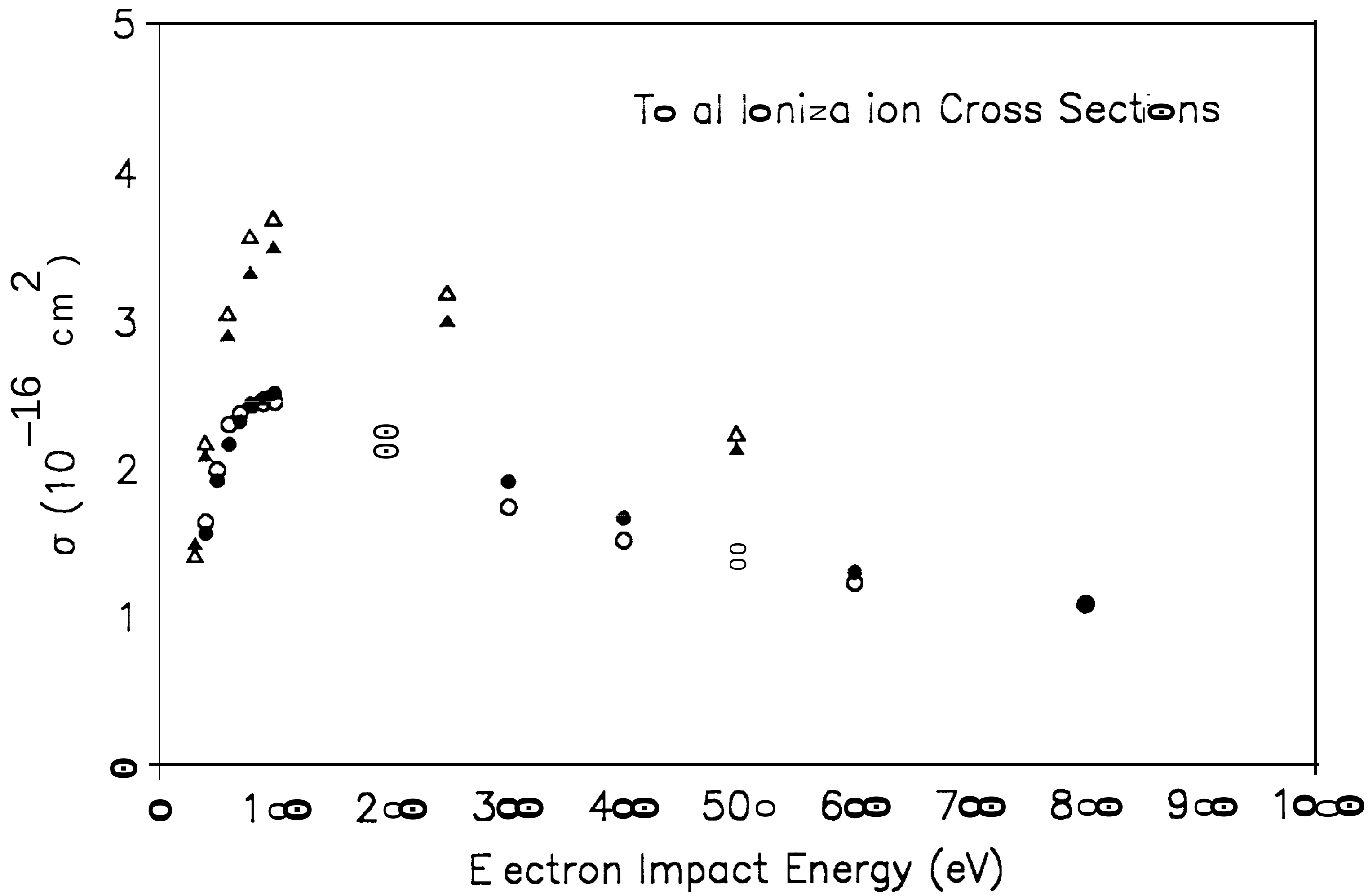

PHA
TAC
SCA
CFD
STOP
START
TAC / SCA
e⁻–BEAM PULSER
TIME DELAY
TIME DELAY
AMP
PULSER
ELECTRON GUN
FLOWMETER
Torr
GAS
TIME OF FLIGHT
MASS SPECTROMETER
GAS INLET VALVE
e⁻
CAPILLARY
ARRAY
PARTICLE
DETECTOR
ION TRANSPORTING LENSES
INTERACTION
REGION
EXTRACTION
VOLTAGE
FARADAY CUP



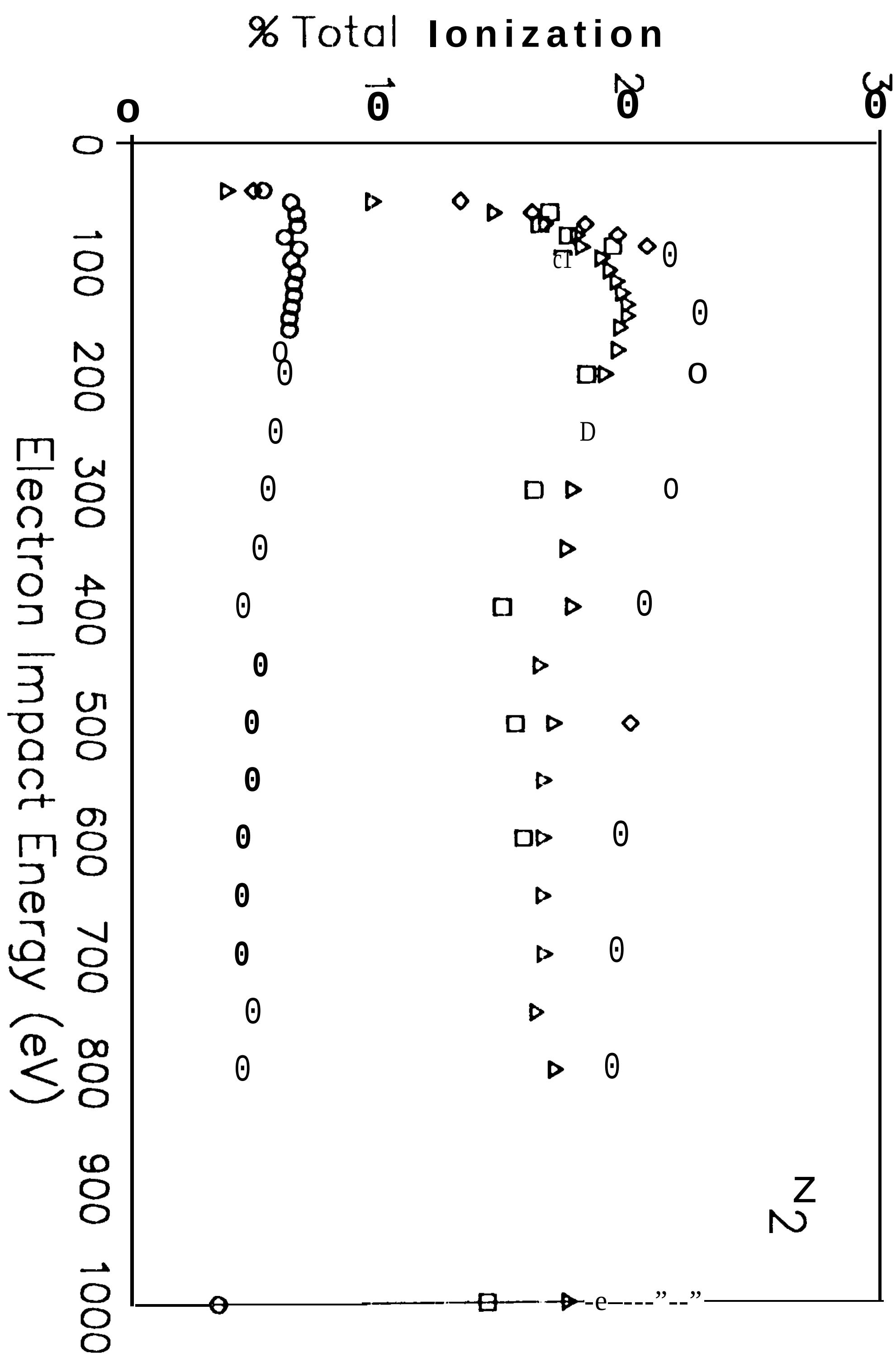
N2 (70 eV)
Crossed-beam
(a)
a
N+ (fast)
b
N+ (slow)
X (10)→
c
N2+
(b)
Static-gas
c
b
(x10)→
1
Intensity (arb. units)
14.0
Time of fight (microseconds)



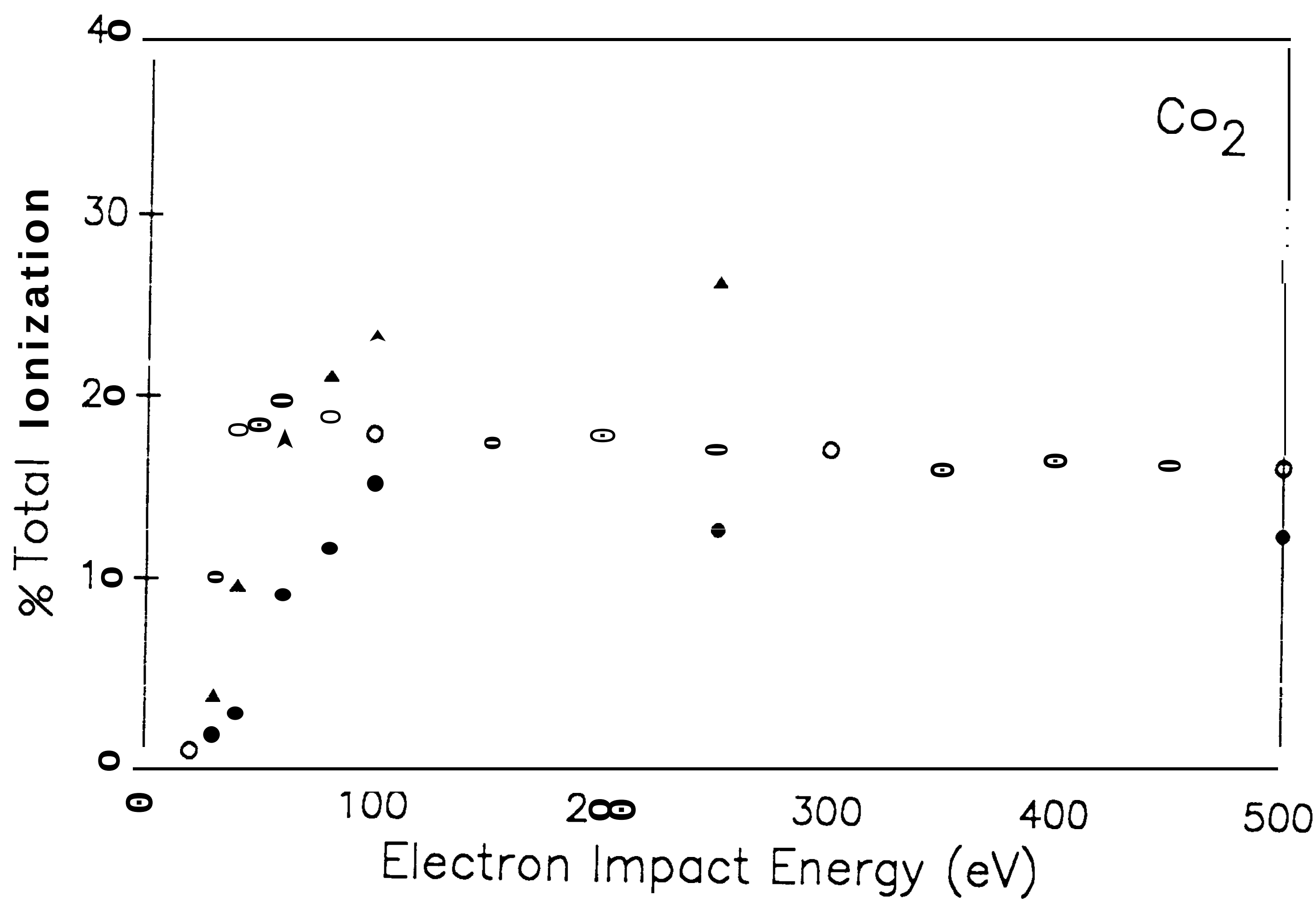
CO2 (300 eV)
Crossed-beam
(a)
C+
O+(fast)
O+(slow)
CO2++
CO+(fast)
CO+(slow)
CO2+
←-(x10)
Static gas
(b)
a
b
c
d
e
f
g
←-(x10)
1
1
10.0
14.0
18.0
Intensity (arb. units)
Time of flight (microseconds)



To al Ioniza ion Cross Sections
σ (10−16 cm2)
0
1
2
3
4
5
0
100
200
300
400
500
600
700
800
900
1000
Electron Impact Energy (eV)



% Total Ionization
0
10
20
30
0
100
200
300
400
500
600
700
800
900
1000
Electron Impact Energy (eV)
N2



% Total Ionization
40
30
20
10
0
0
100
200
300
400
500
Electron Impact Energy (eV)
Co2